

# **Experimental studies of Phase Equilibria in Systems of Natural Gas**

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## **ABSTRACT**

PT<sub>px</sub>-measurements of phase equilibria in natural gas mixtures containing nitrogen, methane, ethane and helium are made in the temperature range from 100 to 270 K and pressures up to 10 MPa. Experimental results from a VLE apparatus for the binary systems of nitrogen-ethane and methane-ethane are shown. In addition to this VLE-apparatus, a new apparatus for the measurement of VLLE is presented which provides complete data sets for up to three equilibrium phases including all saturation densities.

*Keywords:* Experimental method; vapor-liquid-(liquid-) equilibria; data; densities; mixtures; natural gas.

## **1. INTRODUCTION**

The optimal design of the processes of liquefaction, separation, storage, pumping and transport of natural gas requires accurate equations for the calculations of the thermophysical properties. The development of effective equations demands correspondingly accurate experimental data of the gas and liquid phases and the phase equilibria. Although several studies have been performed to provide experimental data

for mixtures containing natural gas constituents, there are shortcomings with regard to the availability of accurate data sets for certain ranges of temperature, pressure and composition and a scarcity of data of saturation densities.

For that reason, comprehensive PT<sub>px</sub>-measurements of phase equilibria of mixtures containing the major constituents of natural gas, nitrogen, methane, ethane and helium are carried out in our laboratory. Experimental results of the vapor-liquid equilibria in the binary systems of nitrogen-ethane and ethane-methane are presented in this paper.

Many of the nitrogen-rich systems of natural gas at low temperatures exhibit vapor-liquid-liquid equilibria. So a new apparatus was developed which allows the investigation of both, VLE and VLLE at low temperatures including the accurate measurement of all three saturation densities. Details of this new VLLE –apparatus are given in this work.

## **2. VLE MEASUREMENT**

### **2.1 Apparatus**

The used VLE-apparatus is schematically shown in Fig.1. A detailed description of this apparatus is given by Schulze [1, 2]. The equipment assembly consists of two main parts, the equilibrium cell with the Pt25 platinum resistance thermometer and the liquid circulation loop. The pressure receiver, the safety device and the gas sample valve are located on the top of the equilibrium cell. The liquid circulation loop contains the circulation pump and the liquid sampling system. The apparatus is cooled by liquid nitrogen pumped through three separate circuits of cooling coils. These coils are connected with electric resistance heaters to control the temperature. To minimize the

heat exchange, the apparatus is placed in a vacuum chamber and surrounded by radiation shields.

The pressure is measured indirectly by using the pressure receiver and a piston manometer (Desgranges & Huot, Model 21410) as described in [1, 3].

After equilibrium has been reached, the liquid sample can be separated in the sampling tube of well known volume by closing the corresponding valves. To avoid vaporization of the liquid, the temperature in the circulation loop can be adjusted slightly below the equilibrium temperature. A vent pipe guarantees that there are no gas bubbles in the sample. Gas sample and liquid sample are withdrawn, weighed and afterwards analyzed by gas chromatography (HP 5880A). The density of the liquid phase can be determined directly by  $\rho' = (m/V)_{\text{sample}}$ . The vapor density is calculated based on mass balances [1].

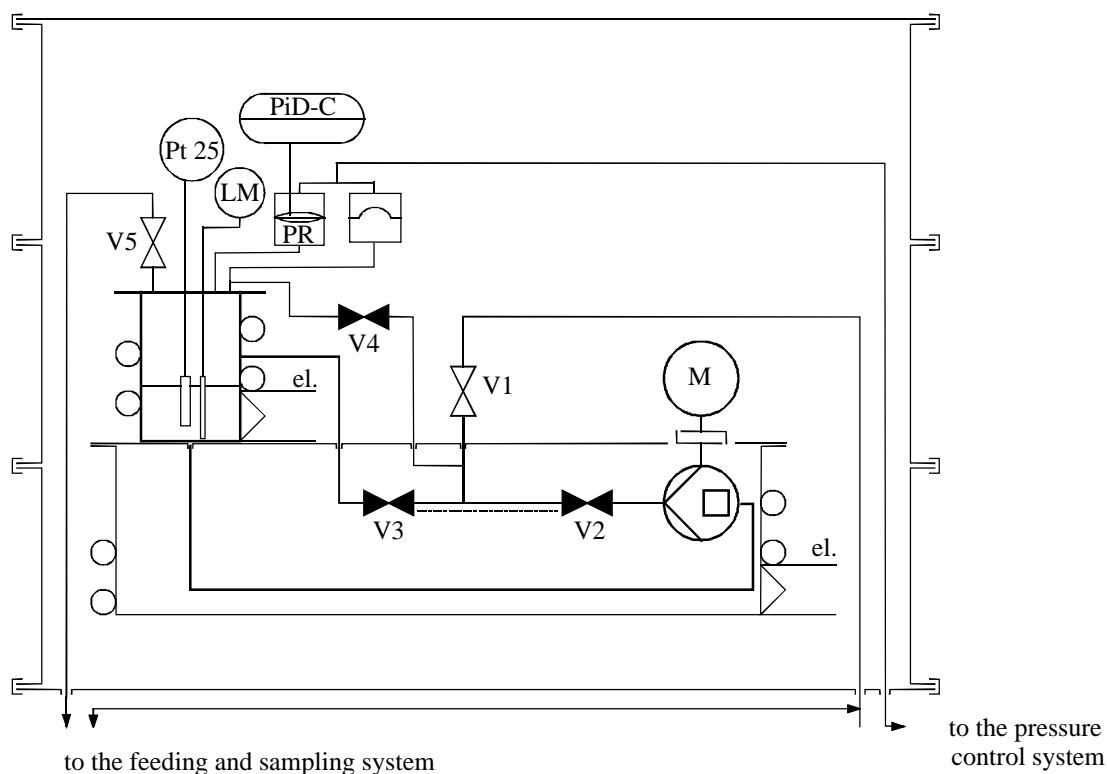


Fig.1 Schematic diagram of the VLE-apparatus

## 2.2 Experimental results

Comprehensive PTpx-measurements have been carried out in binary systems containing nitrogen, methane and ethane under contract for the GERG-project 'Reference Equation for Natural Gas'. To give an idea of the ongoing experimental work in our laboratory, some data of the binary systems of nitrogen – ethane and methane – ethane are presented in this paper. The data for the vapor-liquid-equilibrium in the system nitrogen-ethane at 210K and 270K are presented in Table 1. Results for the system methane – ethane at the 240K and the 270K isotherm are shown in Table 2.

The experimental uncertainties of the data were estimated to

$$\Delta T = \pm 5 \text{ mK} ; \quad \Delta P / P = 0.07 \dots 0.02\% ; \quad \Delta x = \pm 0.005 \text{ mol/mol}$$

$$\Delta \rho' / \rho' = \pm 0.4 \dots 0.7\% ; \quad \Delta \rho'' / \rho'' = \pm 2 \dots 4\% .$$

T [K]	P [MPa]	$x_{N_2}$ [mol/mol]	$y_{N_2}$ [mol/mol]	$\rho'$ [kmol/m <sup>3</sup> ]	$\rho''$ [kmol/m <sup>3</sup> ]
209.927	1.1471	0.0235	0.6668	17.1237	0.6823
209.930	2.0607	0.0521	0.7864	17.2594	1.2598
210.022	3.0401	0.0809	0.8313	17.3509	1.9133
209.815	5.0357	0.1477	0.8629	17.4887	3.3309
210.012	9.9986	0.3309	0.8566	17.3954	7.5426
269.938	3.2681	0.0304	0.2305	13.5010	1.9781
270.013	4.1864	0.0599	0.3357	13.4339	2.5731
269.998	5.7557	0.1131	0.4295	13.2289	3.6194
269.907	8.0147	0.1967	0.4665	12.5121	5.5806
270.000	8.9229	0.2501	0.4578	11.8676	6.6010
269.877	9.0103	0.2545	0.4529	11.7554	6.7706

Tab.1 Experimental results of the binary system nitrogen - ethane

T [K]	P [MPa]	x <sub>CH<sub>4</sub></sub> [mol/mol]	y <sub>CH<sub>4</sub></sub> [mol/mol]	ρ' [kmol/m <sup>3</sup> ]	ρ'' [kmol/m <sup>3</sup> ]
239.994	1.5239	0.0591	0.3481	15.4225	0.9564
240.001	4.4221	0.3684	0.7248	14.9146	3.3146
239.871	5.3739	0.4768	0.7508	14.4691	4.3716
240.000	6.5669	0.6215	0.7476	12.4377	7.2207
270.058	2.8360	0.0505	0.1802	13.5834	1.8713
270.038	2.9075	0.0566	0.1997	13.5938	1.8653
269.974	4.1098	0.1599	0.3870	13.1945	2.7518
269.993	4.8145	0.2180	0.4368	12.8938	3.5502
269.835	6.0136	0.3276	0.4917	11.8150	5.0443
270.001	6.6263	0.4258	0.4498	9.1583	7.6179

Tab. 2 Experimental results of the binary system methane - ethane

The experimental data were compared with predictions using the equation of state by Peng and Robinson [4] and the mixing rule proposed by Shibata and Sandler [5] with two binary interaction parameters  $k_{ij}$  and  $d_{ij}$ . The interaction parameters were fitted to experimental data in the temperature ranges of interest using the objective function

$$\sum_{i=1}^N \left[ \left( \frac{P_{cal,i} - P_{exp,i}}{P_{exp,i}} \right)^2 + (y_{lcal,i} - y_{lexp,i})^2 \right] = \min \quad (1)$$

The experimental data given in Table 1 and 2 and the results of the correlation based on the Peng-Robinson-EOS are depicted as P-x diagrams in Fig. 1 and 2. Within the above mentioned degree of uncertainty, the experimental data are in good agreement with the prediction .

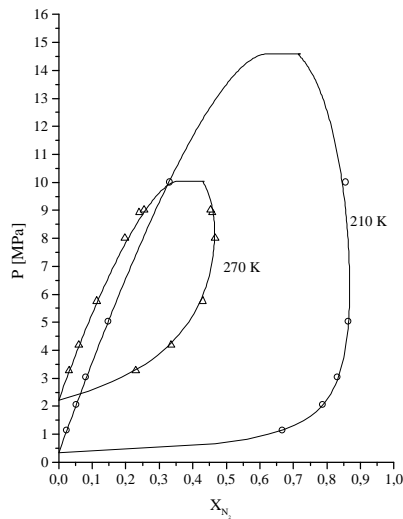


Fig. 2 Isothermal phase equilibria in the binary system nitrogen-ethane: O,  $\Delta$  = experimental data; curves = calculations with the Peng-Robinson EOS and Shibata-Sandler mixing rule  
( $k_{12} = k_{21} = -0.00134$  ;  $d_{12} = d_{21} = -0.033882$ )

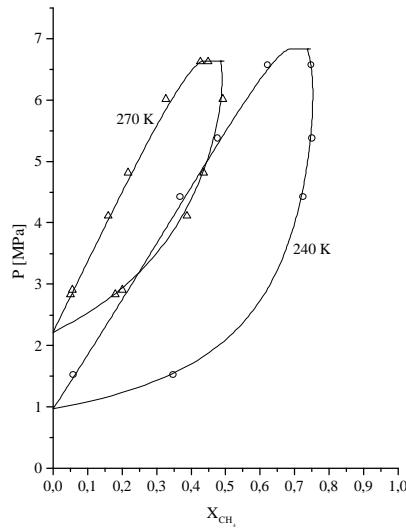


Fig. 3 Isothermal phase equilibria in the binary system methane – ethane: O ,  $\Delta$  = experimental data; curves = calculations with the Peng-Robinson EOS and Shibata-Sandler mixing rule  
( $k_{12} = k_{21} = 0.00166$ ;  $d_{12} = d_{21} = 0.000314$ )

### 3. NEW APPARATUS FOR VLLE MEASUREMENT

#### 3.1 General description

The schematic diagram of the new VLLE-apparatus which was designed for a temperature range between 100 and 300 K and pressures up to 10 MPa is shown in Fig. 4. In general, it is similar to the old VLE-apparatus, but it includes significant modifications and extensions. The apparatus uses recirculation – sampling loops for each phase and the most important improvement is the integration of a single-sinker-densimeter in the gas circulation loop for the measurement of the saturation vapor density. The components of the liquid circulation loops are similar to those of the VLE-

apparatus. The liquid densities are determined by the mass of the samples and the volume of the sampling tubes as described in Section 2.1. The equilibrium cell is additionally equipped with a stirrer and an optical inspection device. More detailed descriptions of the equilibrium cell and the gas recirculation loop are given in the following sections.

A sample of each equilibrium phase can be obtained by closing the corresponding valves to block off sections of the circulation loops without affecting the equilibrium by a pressure drop. All valves in the recirculation loops are specially designed and finely adjustable .

The temperature is determined by a platinum resistance thermometer Pt25 (Rosemount), calibrated to the ITS-90 by the PTB in Berlin. The resistance of the Pt25 is measured by a self adjusting resistance bridge (ASL Model F17) against a  $25\ \Omega$  comparison resistance (Tinsley). The pressure is measured indirectly in a similar way as described by Kleiber [3], but with some modifications in the pressure measurement and control system which will be explained in section 3.4.

To assure homogeneous temperature distribution, all components within the circulation loops are made of copper or brass and placed in a vacuum chamber. These components which connect the apparatus with the outside environment of the vacuum chamber are made of stainless steel. The apparatus is also cooled by liquid nitrogen pumped through cooling coils of copper tubing. These cooling coils are connected with electric resistance heaters for the fine adjustment of the temperature and are arranged in four circuits having separately controlled temperature zones. To achieve the correct temperature adjustment and to control the temperature distribution in the apparatus, a number of Pt100 - thermometers are placed within the system.

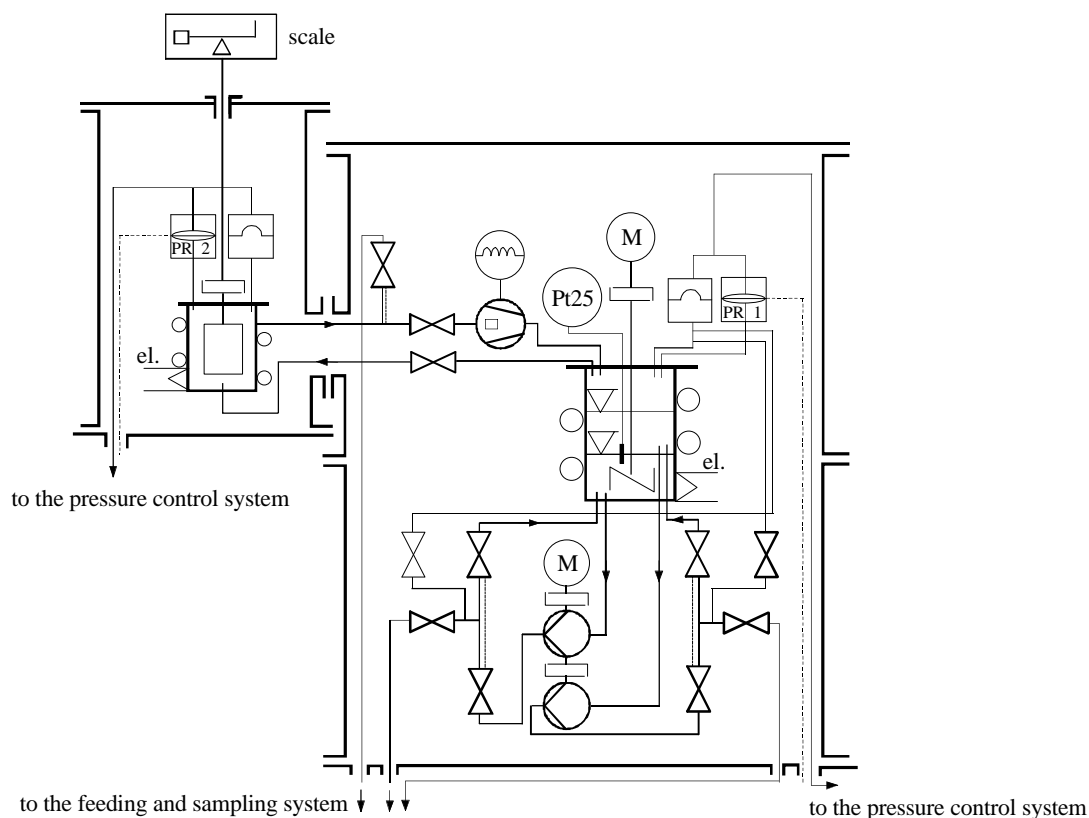


Fig. 4 Schematic diagram of the VLLE-apparatus

### 3.2 Equilibrium cell

A cross sectional view of the equilibrium cell made of copper is shown in Fig. 5. It has an internal volume of approximately  $700 \text{ cm}^3$  and is closed at the top by a flange.

The Pt25-thermometer is placed in a well inside the cell. This well, the pressure receiver and the safety device as well as the inlet and outlet of the gas phase are screwed into the flange. The bottom of the equilibrium cell is connected with the liquid circulation loops. To ensure that the liquid phases are not mixed in the circulation loops when sampling takes place, the inlet and outlet of the liquid with the lower density is positioned at a fixed distance above the bottom. This means that the lighter liquid phase must be positioned at the appropriate level. For controlling the location of the liquid-liquid interface and observation of the phase separation, the equilibrium cell has an optical



inspection device similar to the one described by Kremer [6]. An endoscope (Claasen & Co) can be introduced into a well which is sealed with a melted high-pressure glass window (METAGLAS). To minimize reflection, the fibrelight cable which illuminates the cell is introduced separately into a second well. A cold light source with an aperture is used to reduce the heat input into the cell by the light.

As the recirculation loops are used for sampling and density measurement and not for mixing, an internal stirrer is required to assist the equilibrium process. The stirrer is driven from the top with a magnetic clutch rotated by a modified miniature DC-motor (Faulhaber) outside the equilibrium cell.

The equilibrium cell is cooled by two cooling coils which are arranged in a countercurrent way to minimize the temperature gradient. The electric resistance heater for the fine adjustment of the temperature is wound in a groove around the equilibrium cell.

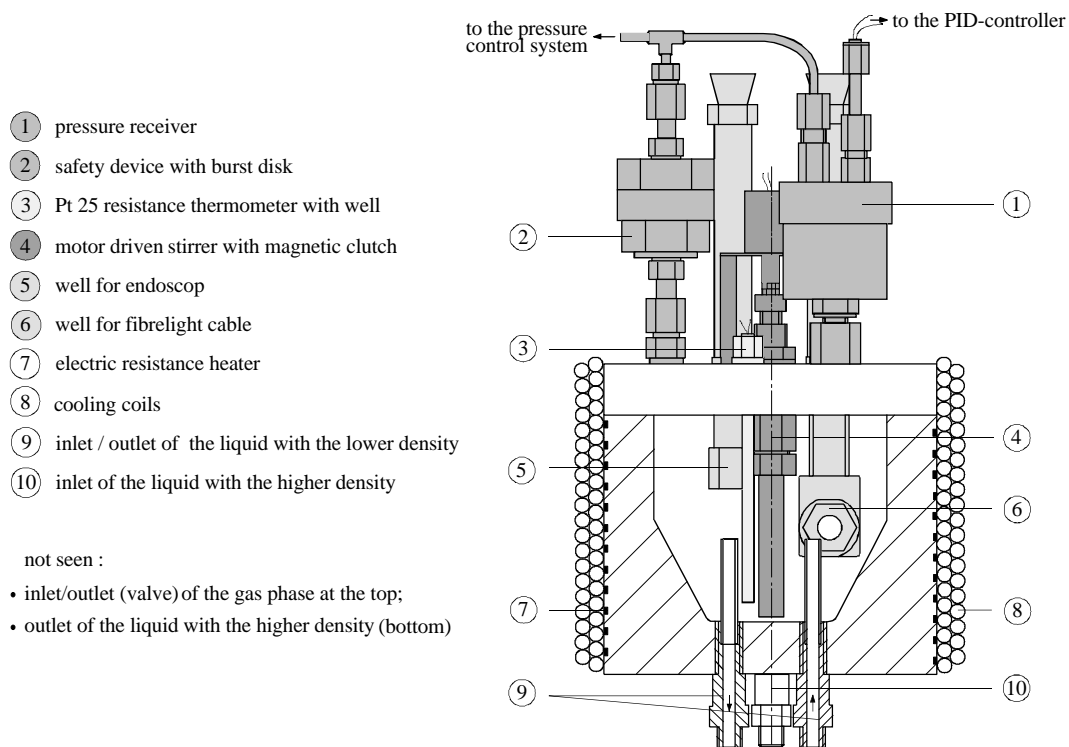


Fig. 5 Cross sectional view of the equilibrium cell

### 3.3 Gas recirculation loop

The most important improvement of the VLLE-apparatus is the supplementation of a gas circulation loop. The integration of a second cell, called the vapor cell, with a single-sinker-densimeter (Rubotherm) allows the direct measurement of the vapor density. The vapor phase flow is driven by a piston pump consisting of a reciprocating permanent magnet and a solenoid coil. A schematic drawing of the pump similar to the one used by Fleck et. al [7] is shown in Fig 6. To minimize pulsation, the vapor is divided into two streams while flowing through the double acting pump. The solenoid induces the upward motion of the magnetic piston in the tube while the piston falls down by gravity at the end of the electrical pulse. Thus an electrical pulse is only needed for a half period, reducing the heat dissipation of the solenoid coil.

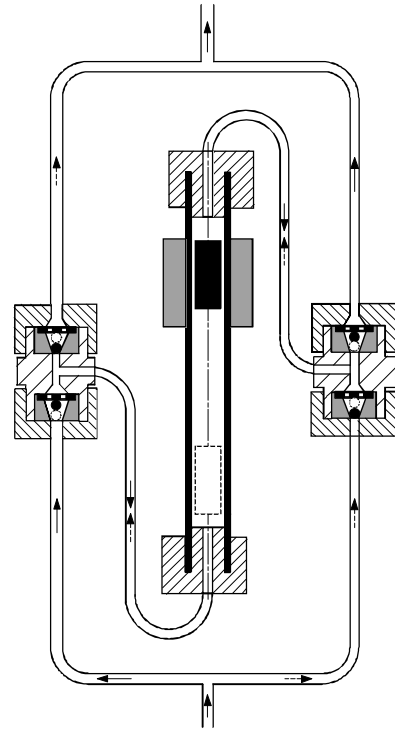


Fig. 6 Schematic drawing of the piston pump

To avoid condensation on the sinker, the pressure in the vapor phase cell is kept slightly below the pressure of the equilibrium cell with the help of a valve and the piston pump. To control this pressure, the vapor cell is equipped with a pressure receiver and a safety device. Condensation of the circulating vapor stream is additionally avoided by having a separately controlled temperature zone as mentioned above. Thus the temperature in the vapor circulation loop can be adjusted at a slightly higher value than the equilibrium temperature.

### 3.4 Pressure control system

The pressure is determined indirectly as already described in [1, 3] by using a pressure receiver connected with the equilibrium cell in which a membrane separates the equilibrium pressure from the reference pressure. A pressure difference causes a deflection of the membrane and an inductive motion transducer yields the input signal for the pressure control system to compensate the reference pressure. After a zero balance between equilibrium and reference pressure has been reached, the pressure can be determined by the piston manometer in the control system. For controlling and measuring the pressure difference between the equilibrium cell and the vapor cell, the vapor cell has been equipped with a second pressure receiver, and a parallel reference line has been added to the pressure control system as shown in Figure 7. After achieving zero balance between the respective reference pressure and the pressure in the corresponding cell, the difference can be determined by a differential-pressure transmitter (Fisher-Rosemount).

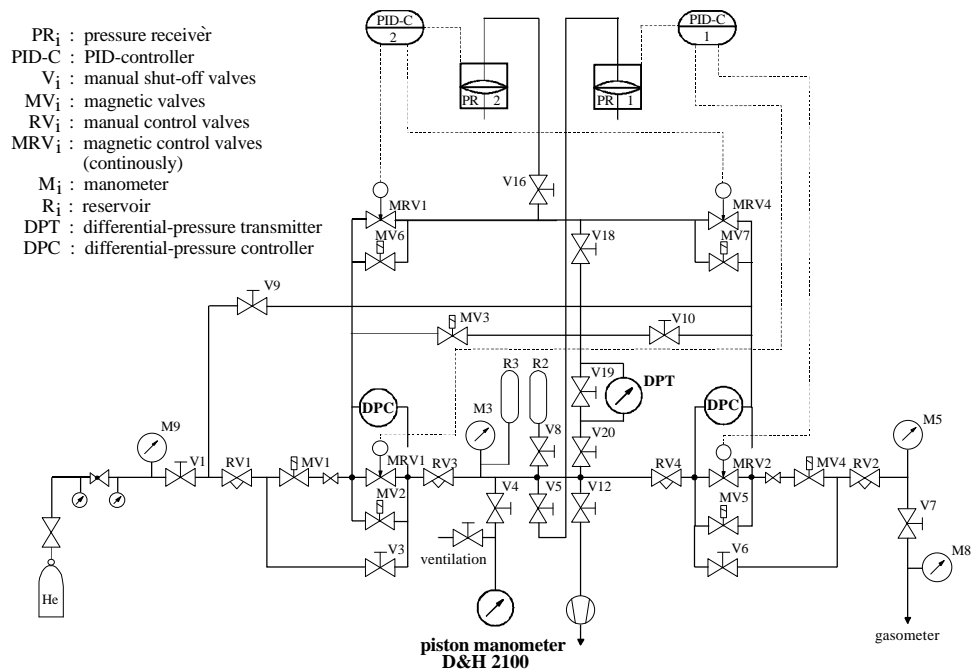


Fig. 7 Pressure control system

#### 4. CONCLUSION AND FUTURE WORK

In this paper two experimental apparatuses for the measurement of phase equilibria in natural gas systems have been presented. Some experimental results for vapor-liquid equilibria in the binary systems of nitrogen – ethane and methane - ethane have been shown. Future work will be done for measurement of VLE in the ternary system nitrogen – methane – ethane and in multicomponent systems of natural gas containing helium. The VLE measurement will be complemented by measurements of VLLE in the systems nitrogen – ethane and nitrogen – methane – ethane.

#### 5. LIST OF SYMBOLS

$d_{ij}, k_{ij}$	interaction parameters of the mixing rule
EOS	equation of state
$i$	number of an experimental point
$N$	total number of experimental points
$P$	pressure [MPa]
$T$	temperature [K]
VLE	vapor-liquid-equilibrium
VLLE	vapor-liquid-liquid-equilibrium
$x$	(liquid) mole fraction
$y$	vapor mole fraction

##### 5.1 greek letters

$\rho'$	molar density of the liquid phase [kmol/m <sup>3</sup> ]
$\rho''$	molar density of the vapor phase [kmol/m <sup>3</sup> ]

## 5.2 subscripts

cal.                calculated

exp.                experimental

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